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Microstructural Investigations on Alloy Mg-2Ca-0.2Mn-0.5Zr-1Y

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Abstract. Authors elaborated a five component material using specific magnesium master alloys with several elements resulting a potential biocompatible and biodegradable alloy.The main goal of the present paper is to investigate the properties of some master Mg-2Ca-0.2Mn-0.5Zr-1Y alloy. The surface morphology was characterized using X-ray diffraction (XRD), optical microscopy and scanning electron microscopy (SEM). After the XRD analysis, it have been identified the following compounds, such as Mg, Mg_2Ca, $Mg_{24}Y_5$, respectively MgY. These compounds have the hexagonal crystallographic structure for Mg and Mg_2Ca type, respectively cubic form for Mg-Y and $Mg_{24}Y_5$. The microstructure presents a uniform morphology and an undisclosed zirconium. Also, manganese is embedded in magnesium and Ca forms a lamellar eutectic mixture of Mg_2Ca type. In conclusion, Mg-2Ca-0.2Mn-0.5Zr-1Y alloy shows similar characteristics from the microstructure point of view with other biodegradable materials, these alloy could be used as biodegradable implant.

1. Introduction

Magnesium alloys are widely used in the automotive industry, in the medical and aerospace industries due to their low density, high specific strength, good pouring capacity and machining [1-5]. By comparing with other commonly used biomaterials [18,19], magnesium and its alloys have excellent biocompatibility and biodegradability as well as a more elastic modulus near that of human bones and a possibility of gradual dissolution and absorption after implantation in a physiological environment. Although they are so used, their corrosion and wear resistance limits the field of application of Mg to other industries. Moreover, the rate of degradation of these alloys in the corrosive environment, especially in the Cl-containing physiological environment, is so rapid that implants cannot maintain their mechanical integrity before restoring human tissue [11-13]. Therefore, Mg align with other elements to increase corrosion resistance. Mg alloys have attracted particular attention with regard to the degradability of the implanted materials due to their high biocompatibility and satisfactory mechanical properties. As a result, Mg alloys have the advantage that they do not exhibit the stress-shielding effect normally occurring in conventional metal implants made of stainless steel or titanium choices that are widely used for bone implants [6,8,16]. Various Mg alloys have been investigated as biodegradable materials and some have shown good biocompatibility, such as Mg-Ca, Mg-Zn, Mg-Mn, Mg-Zr, Mg-Y [17]. In the paper presented Mg-2Ca-0,2Mn-0,5Zr-1Y showed specific magnesium microstrusture and good mechanical properties. Mn is mainly used to increase ductility. In Mg-Ca binary alloys, the Mg_2Ca

phase is formed, which can improve creep resistance due to solid solution consolidation, precipitation consolidation and grain boundary fixation. Higher amounts of Ca (> 1% by weight) can lead to problems such as hot breakage or sticking during casting [14]. The RE elements can stop the grain boundaries at high temperatures and can help increase resistance, especially by strengthening the resistance. Mg-Y alloys are known to form three different intermetallic phases at different temperature intervals with the increase in Y: $Mg_{24}Y_5$, Mg_2Y and MgY [15]. This mechanism increases the operating temperature of Mg alloys in the transport industry and improves creep resistance and corrosion resistance [13]. However, the rate of rapid degradation of Mg choices in human bio-medical limits their clinical applications [9,10]. It is therefore important to improve the corrosion resistance of Mg alloys in order to broaden the field of application. The results will allow us to provide useful data for understanding these intermetallic and designing alloys based on Mg-2Ca-0,2Mn-0,5Zr-1Y high performance.

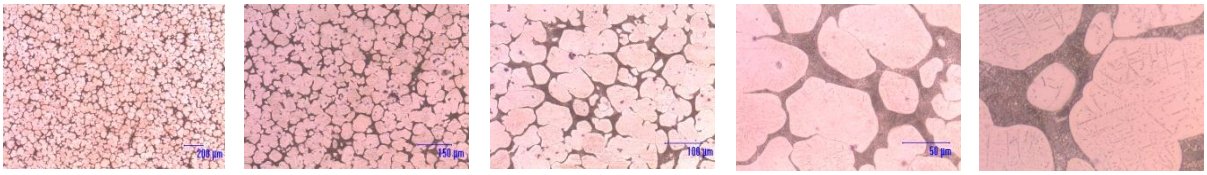
2. Materials and methods

The samples used in this experiment were prepared by blending the corresponding proportions of commercial Mg ingots (& gt; 99.95%) and 4 master alloys Mg-25% Y, Mg-15% Ca, Mg-3% Mn and Mg-25% Zr. Experimental compositions of Mg-2Ca-0.2Mn-0.5Zr-1Y were prepared. These compositions were prepared using an induction furnace at 750°C under the protection of an inert atmosphere (Ar), the graphite crucible was allowed to cool to room temperature after which it was broken to obtain a 50 mm ingot and Diameter of 20mm this ingot was cut into pills with a diameter of 20mm and a thickness of 5 mm. The samples were sanded with abrasive paper with grain size up to 2000 SiC to obtain a uniform smooth surface. The microstructures were investigated by scanning electron microscopy (SEM Quanta 200 3D) equipped with an EDX detector. The analyzed area of each sample was milled and polished to a final finishing with a alumina suspension of 0.05 lm. Prior to observation, the samples were etched using 4% w / w nitric acid in ethanol for 5-8 s, washed thoroughly with water and alcohol and then dried with hot air. To highlight microstructures, use the Leica 5000DMI optical microscope. We used an XRD Expert Pro MPD diffractometer for diffraction. The microhardness was done using a tribometer with indentation and scratch. The micro scratch test was carried out as follows: a constant load of 5N was applied over a distance of 4mm with a displacement velocity of 0.1mm / s.

3. Results and discussions

3.1. Structural analysis

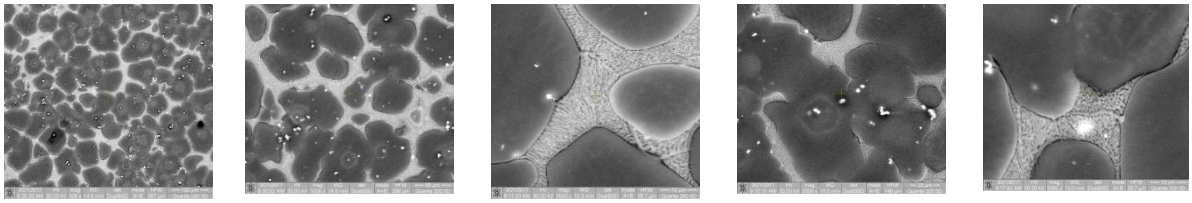
3.1.1.Optical images. The images shown below represent the morphology of the analyzed sample area, captured at the Leica 5000DMI microscope at different magnification powers, and show high material compaction.



a) b) c) d) e)

Figure 1. Optical analysis of the material.

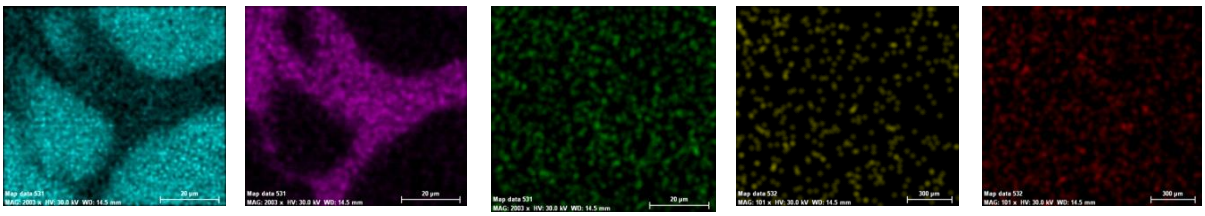
3.1.2. Scanning electron microscopy. The aspects of morphology and microstructure are presented in figure 2 (a, b, c, d, e). The SEM images taken at up to 5000x highlight the phases of Mg alloys after casting and the compactness and homogeneity of the material and surface morphology. The grains formed after casting the four alloys have different shapes depending on the alloy that predominates in a certain area.



a) b) c) d) e)

Figure 2. Surface SEM images for Mg-2Ca-0,2Mn-0,5Zr-1Y.

3.1.3. EDX analysis. To see the estimative composition of Mg choices after SEM, an EDX analysis followed and the results obtained after the test are shown in figure 3. After the EDX test we found that MgY has a Y-concentration of 24.790%, Mg-Zr 19.636%, Mg-Mn 1.537% and Mg-Ca 16.835.



a)Mg b)Mg-15Ca c)Mg-3Mn d)Mg-25Zr e)Mg-30Y

Figure 3. EDX images of Mg alloys.

3.2. XRD analysis

The Xrd analysis was performed on a Panalytical XPERT Pro MPD diffractometer, CuKα X-ray.

Table 1. Lattice parameters of Mg-2Ca-0,2Mn-0,5Zr-1Y.

Compound	Space Group	Crystal system	a (Å)	b (Å)	c (Å)	α (º)	β (º)	γ (º)	Cell volume (10^6 pm^3)
CaMg2	P63/mmc	Hexagonal	6,2300	6,2300	10,1200	90	90	120	340,16
Mg	P63/mmc	Hexagonal	3,2200	3,2200	5,2300	90	90	120	46,96
Mg24Y5	I-43m	Cubic	11,2500	11,250	11,2500	90	90	90	1423,83
MgY	Pm-3m	Cubic	3,8000	3,8000	3,8000	90	90	90	54,87

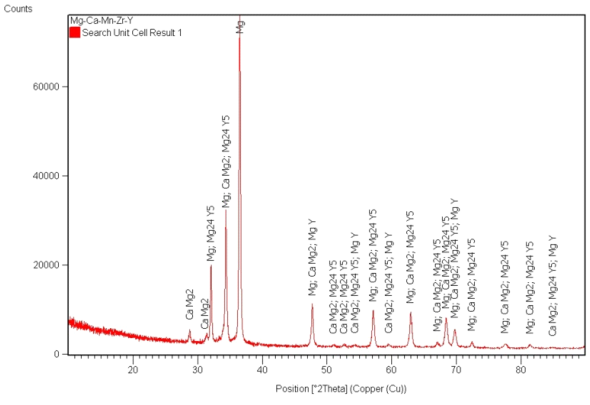
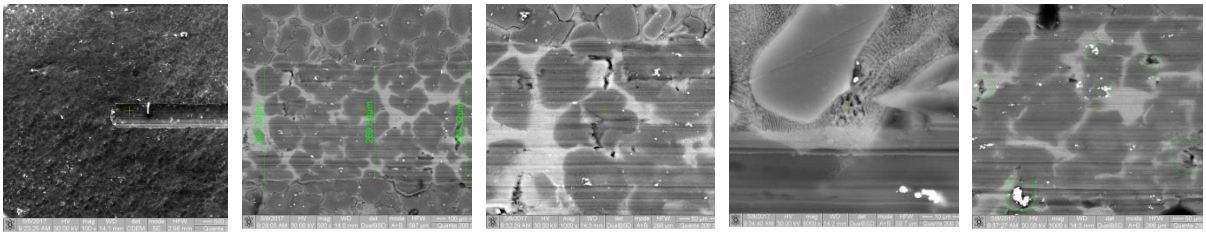


Figure 4. Graph of Xrd analyzes for Mg-2Ca-0,2Mn-0,5Zr-1Y.

The XRD models are shown in figure 4, Pure Magnesium is highlighted at 33.46° (2 Theta - as the highest peak). There has been highlighted the Mg_2Ca and $Mg_{24}Y_5$ and MgY compounds first having the hexagonal crystallographic structure and the other two crystallographic cubic structures. Mg-Mn and αZr or less revealed they have the same hexagonal crystallographic structure as the Mg. Parameters of all compounds are shown in table 1.

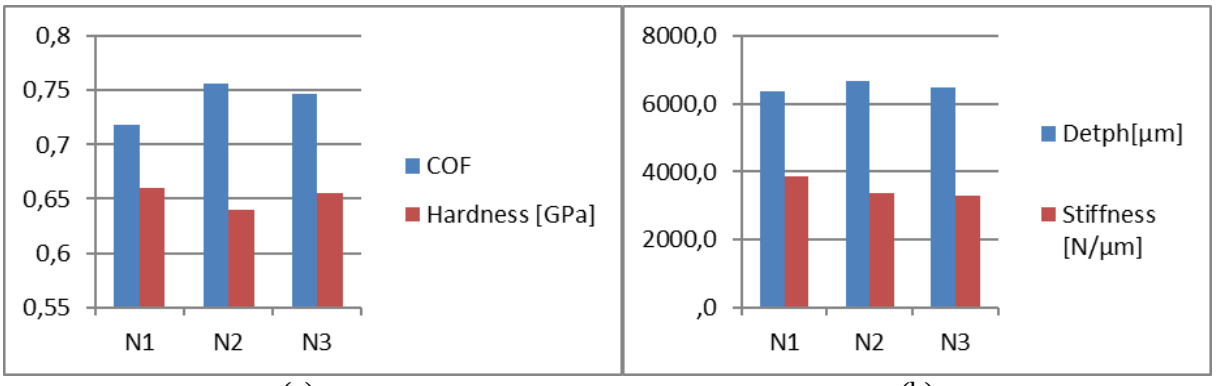
3.3. Scratch and micro-indentation analysis

Figure 5 shows a scratch test of the Mg-2Ca-0.2Mn-0.5Zr-1Y sample. Three attempts were made in 3 different areas, resulting in small differences between them, which show the influence of alloying elements in different areas. Table 2 shows the values for young modulus, hardness, scratch, coefficient of friction and stiffness for all three tests. The coefficient of friction is rather low about 0.747. The results of the microindentation test showed a depth between 6,372 µm and 6,682 without fracture.

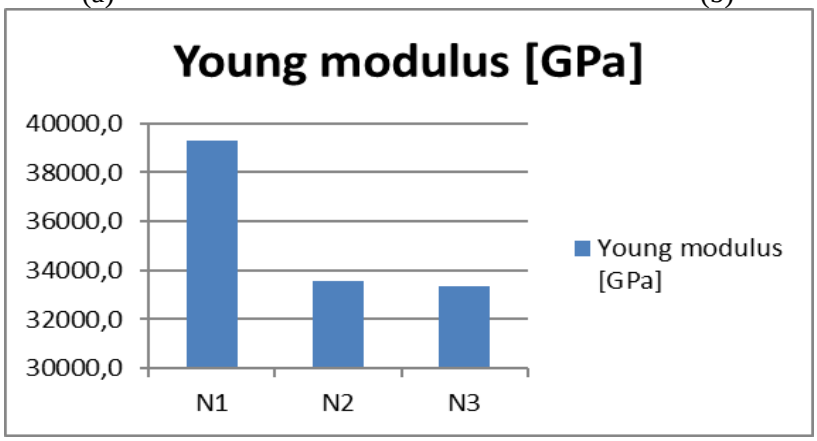


a)100x b)500x c)1000x d)5000x e)1000x

Figure 5. Scratching on diffrent magnifying powers.



(a) (b)



(c)

Figure 6. Young modules.

The penetration trace of the scratch test is not uniform and has different widths as observed in figure 5b, widths between 294.32μm and 269.84μm. This test demonstrates that the material obtained after casting does not have a uniform but well-structured and fairly compact composition.

Figure 5c shows that during scratching, the material breaks to the limit of Mg_2Ca grains and grains of Mg.Because of all the master alloys Mg-Ca has the lowest breaking resistance.

Table 2. Some mechanical properties of Mg-2Ca-0,2Mn-0,5Zr-1Y.

Mg-2Ca-0,2Mn-0,5Zr-1Y	N1	N2	N3
Detph [μm]	6.372	6.682	6.503
Stiffness [N/μm]	3.877	3.383	3.308
Young modulus [GPa]	39.292	33.567	33.371
COF	0.718	0.756	0.747
Hardness [GPa]	0.663	0.647	0.652

The young modulus has a fairly high value of 39,292, but in the following tests it decreases gradually 33,567GPa and then 33,371GPa, which shows us that the casting has a satisfying elasticity and is close to that of the human bone. The hardness of the alloys is rather small but higher than that of pure magnesium.

4. Conclusions

The purpose of the paper was to form a new biodegradable biomaterial formed in the base of Mg and alloyed with several elements such as Ca, Mn, Zr and Y for a high biocompatibility, an increased resistance to corrosion and degradation in time as long as possible. A possible application could be using these materials in medical and not only. Influence of Y shows us greater resistance and at the same time other biodegradable elements in small quantities bring benefits to the human body. Researching morphology, X-ray diffraction, micro scratch and micro indentation, and even the EDX test helps us to improve the material through future studies for the best biocompatibility with the human body. X-ray analysis showed the presence of crystallized compounds: Mg_2Ca, $Mg_{24}Y_5$, MgY, MgMn and αZr having the hexagonal crystalline structure for Mg_2Ca, MgMn, αZr as well as the crystalline cubic structure for $Mg_{24}Y_5$ and MgY. The modulus of elasticity is quite high, which shows us that it is a good thing for Mg-based biodegradable implants. The research of the material will continue with further experiments in order to achieve biodegradable prostheses and implants successfully replacing the classic stainless steel Co-Cr and Ti alloys.

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